

Electric dipole moments of nitric acid-water complexes measured by cluster beam deflection

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Abstract. Water clusters embedding a nitric acid molecule $\text{HNO}_3(\text{H}_2\text{O})_{n=1-10}$ are investigated via electrostatic deflection of a molecular beam. We observe large paraelectric susceptibilities that greatly exceed the electronic polarizability, revealing the contribution of permanent dipole moments. The moments derived from the data are also significantly higher than those of pure water clusters. An enhancement in the susceptibility for $n=5,6$ and a rise in cluster abundances setting in at $n=6$ suggest that dissociation of the solvated acid molecule into ions takes place in this size range.

Keywords: Water clusters, electric dipole moments, beam deflection

PACS: 36.40.-c, 82.33.Fg

INTRODUCTION

One of the most basic phenomena in chemistry is the proton delocalization that occurs when an acid is solvated in water. Strong acids such as HCl are stated to dissociate completely in water, the chlorine ion Cl^- and the proton H^+ separating in the process. Svante Arrhenius, who proposed this electrolytic theory of dissociation, was recognized in 1903 with the Nobel Prize in chemistry. It is understood that the polar water molecules surround the acid and weaken the electrostatic attraction between the positive and negative ions to the point that dissociation becomes energetically favorable. It is an interesting problem to study the onset of this process in water clusters. For example, the minimum number of water molecules required to promote dissolution of HBr was determined experimentally to be five [1, 2] and more recently molecules of HCl were observed to dissociate in the presence of only four water molecules even in the ultra-cold environment of a helium nanodroplet [3, 4].

The electric dipole moment of solvated charge-separated species is expected to be higher than that of the intact molecule [5]. However, even large dipole moments will manifest themselves only as thermally-averaged paraelectric susceptibilities [see Eq. (2) below] when observed at high rotational and/or fluxional temperatures. Thus, for example, in electric-field deviation experiments molecular beams of polar species commonly display weak deflection behavior mimicking that of polarizable (i.e., induced-dipole) particles [6, 7]. Consequently, instead of revealing its dipole moment directly, the onset of dissolution will instead appear in a deflection measurement as a change in the electric susceptibility (effective polarizability). For example, a recent deflection study of sodium-doped water clusters successfully detected the separation of the $3s$ electron and the Na^+ ion via this approach [8]. An early attempt to observe the dissociation transition of a hydrated HNO_3 molecule in a beam was carried out in 1982 [9], but the experimental technique employed a Stark focusing multipole, which is effective for detecting permanent dipoles at low rotational temperatures in low-field-seeking states, but not sensitive to deflections characteristic of induced polarizabilities, which are both weaker and high-field-seeking.

Here we present the results of a beam deflection measurement of the electrical susceptibilities of water clusters containing one nitric acid molecule, and discuss the cluster electric dipole moments derived from these results.

EXPERIMENT

The beam deflection apparatus was previously used to study the electric deflection of water molecules and pure water clusters [10, 11]. To prepare the mixed acid-water clusters, a solution of nitric acid in water is heated inside a stainless steel reservoir, the resulting vapor is mixed with helium that is supplied to the reservoir from an external tank, and

the mixture is allowed to expand into a vacuum chamber through a 75 μm diameter nozzle. The adiabatic cooling of the vapor-helium mixture results in the coalescence of molecules into clusters. The produced distribution of species includes pure clusters of water as well as mixed ones containing one, two or more acid molecules. The beam passes through a skimmer into a second vacuum chamber, where it is collimated and then travels through the region of an inhomogeneous "two-wire" [12] electric field created by a 15 cm long pair of metal electrodes. By applying voltages of up to 27.5 kV between the electrode plates, electric fields and field gradients of up to 80 kV/cm and 380 V/cm², respectively, are created. The field induces an alignment of the clusters' dipole moments, and the gradient gives rise to a net deflecting force on the beam.

The deflected clusters then pass through a rotating chopper and travel to a quadrupole mass analyzer where they are ionized by bombardment with 70 eV electrons, mass selected, and detected by an analog multiplier. The detector output is fed into a lock-in amplifier together with the chopper synchronization pulses. This eliminates noise from the background gases in the chamber and allows determination of the beam velocity from the phase difference between the chopping and detection signals (average $v=1130 \text{ m/s}$ in these experiments).

To determine the beam profiles, a 0.25 mm wide slit is positioned in front of the detector entrance, a distance $L=71 \text{ cm}$ past the middle of the deflection field plates. The slit is scanned across the beam by a stepper motor in steps of 0.25 mm, measuring the intensity at each position with and without voltage applied to the deflection plates.

One of the challenges in a molecular beam experiment like this is to determine the composition of parent clusters from the mass spectra of the ions. Sometimes there is no straightforward way to do so: e.g., in the case of HCl solvated in water clusters the chlorine atom always departs upon ionization [9, 13], so the mass spectrum is indistinguishable from that originating from pure water. Fortunately, in the case of mixed $\text{HNO}_3(\text{H}_2\text{O})_n$ clusters it has been found [9] that the acid is retained upon electron impact ionization, the main fragmentation channel being the loss of one hydroxyl group (just as in the case of pure water clusters). This permits easy identification of the neutral parent.

RESULTS AND DISCUSSION

The first observation to consider is the distribution of cluster intensities. Fig. 1 shows a typical mass spectrum obtained in the present experiments. We observe $(\text{H}_2\text{O})_{m-1}\text{H}^+$ ions deriving from $(\text{H}_2\text{O})_m$ as well as $\text{HNO}_3(\text{H}_2\text{O})_{n-1}\text{H}^+$ peaks corresponding to $\text{HNO}_3(\text{H}_2\text{O})_n$ parents that lost an OH group in the ionization process.

The $\text{HNO}_3(\text{H}_2\text{O})_n$ abundance spectrum reveals a minimum at $n=5$. This feature has been observed previously [9] and interpreted as a possible signal of proton delocalization. The rationale is that a dissociated acid molecule can enhance cluster stability, hence yielding an upturn in intensity for $n \geq 6$.

We now come to the results of the deflection measurement. As an example of the experimental data, Fig. 2 shows the deflection behavior of an agglomerate of one acid molecule and one water molecule. The dashed line corresponds to the beam profile when no electric field is applied. The width of the profile reflects the actual size of the beam due to the finite dimensions of the skimmer and collimator. Once the electric field is switched on, the beam is deflected towards the right, i.e., towards the region of a stronger field. Such uniform deflection without broadening is characteristic of "floppy" species (that undergo internal rotational/vibrational fluctuations, interconverting between different conformations and correspondingly different orientations of their constituent dipoles), as well as of asymmetric rotors characterized by congested rotational Stark spectra [6, 7, 14].

From the magnitude of the deflection, d , one can derive the effective polarizability values for the clusters, α^{eff} , according to the standard equation

$$d = \alpha^{eff} C \frac{V^2}{mv^2}, \quad (1)$$

where m is the cluster mass, v its velocity, V is the applied voltage and C is a calibrated geometrical coefficient [10].

The results for the $\text{HNO}_3(\text{H}_2\text{O})_{n=1-10}$ cluster series are shown in Fig. 3. The sum of the electronic polarizabilities of HNO_3 and $(\text{H}_2\text{O})_n$ are also displayed for comparison. For water $\alpha^{electronic}$ was taken from the calculations in Ref. [15], and for the nitric acid molecule the estimate given in Ref. [16] was used.

Fig. 3 makes it clear that the effective polarizabilities greatly exceed the molecular electronic contribution, revealing the presence of permanent dipole moments. A transitional pattern can be observed in the $n=4-7$ range. The absolute ensemble-averaged dipole moments of the clusters, \bar{p} , can be extracted from the data with the use of the Langevin linear response equation, analogous to that used for pure water clusters and a number of other species [6, 7, 10]:

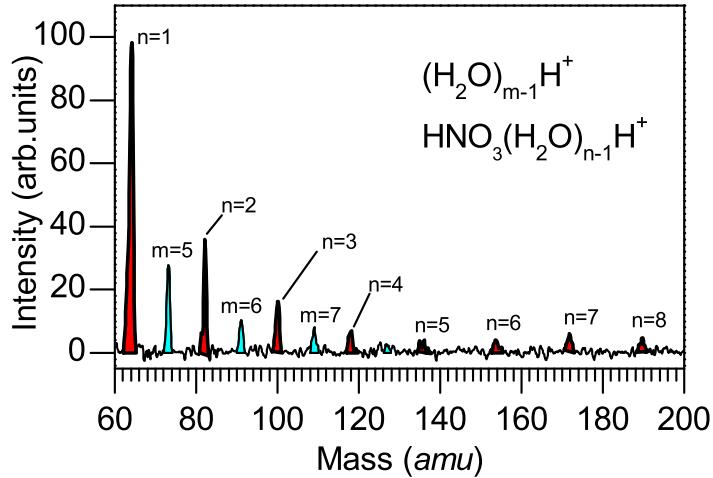


FIGURE 1. Mass spectrum produced by electron ionization of a molecular beam formed by nozzle expansion of a solution of nitric acid in water (concentration 11.2 M) kept in a source reservoir at 70°C and accompanied by helium carrier gas. Indices m and n denote the sizes of the original neutral parent clusters in the beam. Note the non-monotonic trend of the mixed acid-water cluster intensities.

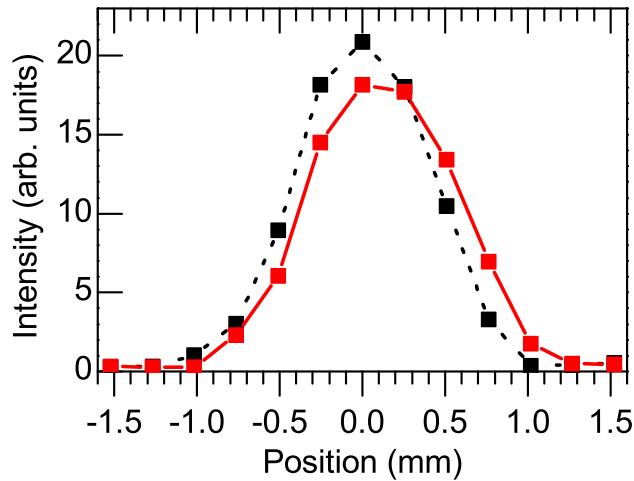


FIGURE 2. A typical cluster beam deflection profile. The illustrated data corresponds to $\text{HNO}_3(\text{H}_2\text{O})$. Dashed line: beam profile without electric field, solid line: with an applied electric field of 80 kV/cm and a gradient of 380 kV/cm². The field produces a deflection towards the right (region of stronger electric field), indicating a susceptibility equivalent to an effective polarizability.

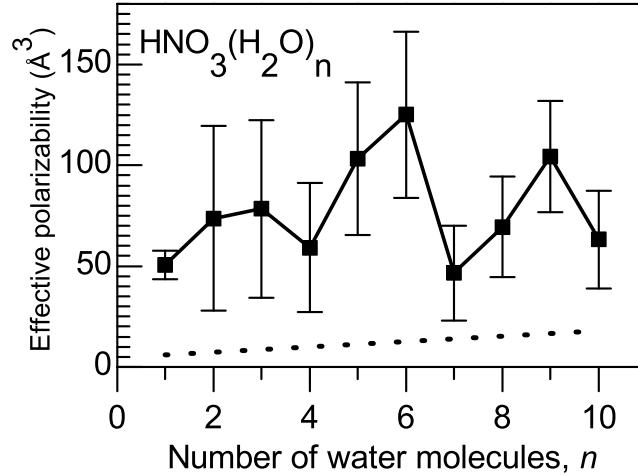


FIGURE 3. Effective electric polarizabilities of water clusters containing one nitric acid molecule (squares). Sum of the electronic contributions to the polarizability from the water clusters and the acid molecule is shown for comparison as a dashed line.

$$\alpha^{eff} = \alpha^{electronic} + \frac{\bar{p}^2}{3k_B T}. \quad (2)$$

We use a cluster temperature of $T=170\text{K}$, which was determined for the conditions of the present experiment from the deflection profile of the water molecule [11], and also found to be consistent with the susceptibility of the pure water pentamer [10].

The derived magnitudes of the dipole moments are shown in Fig. 4. It is important to recognize that the values for $\text{HNO}_3(\text{H}_2\text{O})_n$ significantly exceed those of pure $(\text{H}_2\text{O})_n$ clusters under similar conditions (≈ 1.3 Debye for $n=3-8$ and ≈ 1.6 D for $n=9-10$ [10]).

A comparison with computations available in the literature [17, 18] shows that the experimental results are considerably smaller than the predicted dipole moments, see Table 1. A likely explanation is that whereas theoretical calculations predominantly concentrate on the low-energy isomers of pure and doped water clusters, actual physical systems exist at temperatures high enough that their strongly fluxional nature explores a large number of configurations, producing a reduced average magnitude of the dipole moment. Challenging but important steps to investigate this thermal isomer dynamics would involve theoretical calculations for more realistic conditions, as well as experimental efforts to investigate such free polar species at low temperatures.

TABLE 1. Electric dipole moments of small mixed clusters

Theory (Ref. [17])	Theory (Ref. [18])*	Present results
$\text{HNO}_3(\text{H}_2\text{O})$	4.2 D	1.8 ± 0.2 D
$\text{HNO}_3(\text{H}_2\text{O})_2$	3.8 D	2.2 ± 0.8 D
$\text{HNO}_3(\text{H}_2\text{O})_3$	3.6 D	2.2 ± 0.8 D
$\text{HNO}_3(\text{H}_2\text{O})_4$	0.8-1.8 D	1.9 ± 0.7 D

* Range of values corresponding to several different low-energy isomers

What about signatures of acid dissociation in $\text{HNO}_3(\text{H}_2\text{O})_n$?

As mentioned above, it has been suggested that the uptick in mixed cluster abundances at $n=6$ water molecules may correspond to such a transition.

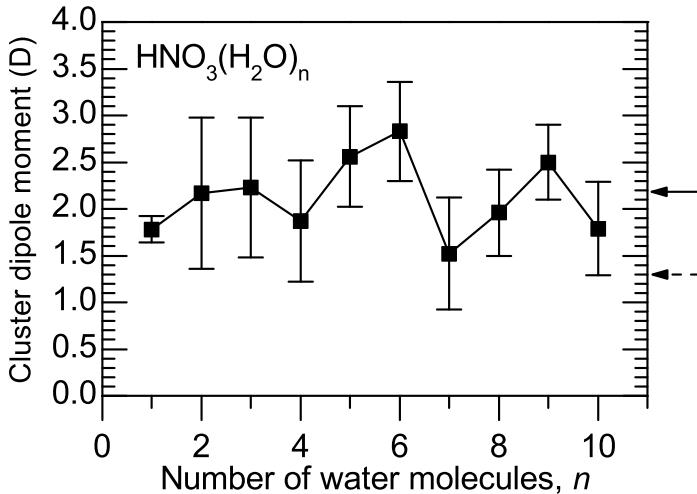


FIGURE 4. Electric dipole moments of mixed clusters deduced using the data in Fig. 3 and Eq. (2). The dipole moment of the gas-phase nitric acid molecule (2.17 D) is shown as the solid arrow [19] and the dipole moment of pure water clusters in the size range $n=3-8$ is shown as the dashed arrow [10].

On the other hand, Scott et al. [18] suggest that the minimum number of water molecules that admit dissociation is $n=4$, with H_3O^+ and NO_3^- ions stabilized by three water molecules that separate them. This cannot be excluded because we do observe a decrease in the dipole moment at $n=4$, but the decrease is small, and the magnitude of the dipole suggests that in actuality a more varied set of configurations may be involved, as commented in the previous paragraph.

The aforementioned alternative expectation that the electric dipole moment of the system should increase when the species becomes charge-separated [5] points instead at a critical size of $n=5$, when there is a noticeable increase in the susceptibility and the corresponding dipole moment. One could argue that adding further water molecules enables them to start surrounding the ions, thereby screening them, reducing the effective dipole moment, and causing the decrease in $\bar{\rho}$ observed for larger species.

Although the present measurement does not point to an unequivocally precise number of water molecules corresponding to the departure of the proton from solvated HNO_3 , one also has to keep in mind that such a solvation step does not have to occur as an abrupt step. It can certainly represent a more gradual structural transition. The abundance and deflection data presented here provide evidence that the acid dissociation takes place in the range between $n=5-6$ in free water clusters of internal temperature of $T \approx 170$ K. It would be very informative to consider, experimentally and theoretically, whether and how this process varies with T .

ACKNOWLEDGMENTS

We would like to thank Dr. D. McGuire for a useful discussion. This work was supported by the U.S. National Science Foundation (PHY-0652534) and by the USC Undergraduate Research Associates Program.

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